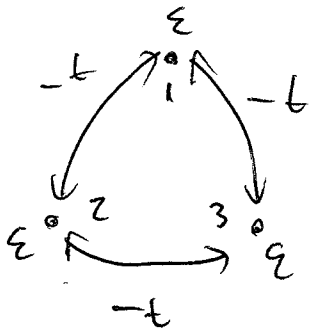
Phys 726 – Assignment 5 Solutions

1. Trihydrogen cation H_3^+ is approximated by two electrons moving between three orbitals on equivalent sites labelled $j=1,2,3$.



The Hamiltonian is

$$\hat{H}_0 = \sum_{\alpha=\uparrow,\downarrow} \sum_{j=1,2,3} \left(-t \left[c^\dagger_{j,\alpha} c_{(j \bmod 3)+1,\alpha} + \text{h.c.} \right] + \varepsilon c^\dagger_{j\alpha} c_{j\alpha} \right)$$

(a) $-t$ is the hopping integral, given by

$$-t \simeq \int d^3r \, \phi(\vec{r} - \vec{r}_j)^* \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi(\vec{r} - \vec{r}_{j'}) \Big|_{\substack{\text{any} \\ j \neq j'}},$$

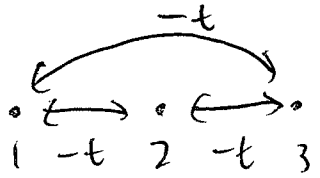
which represents the amplitude for hopping from one site to another.

ε is the energy to occupy the orbital at any of the sites, $\varepsilon \simeq \int d^3r \, \phi(\vec{r})^* \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \phi(\vec{r})$

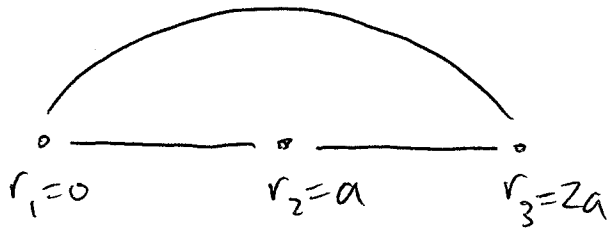
(b) $$\hat{H}_0 = \sum_{\alpha=\uparrow,\downarrow} \Big\{ -t \big[c_{1\alpha}^\dagger c_{2\alpha} + c_{2\alpha}^\dagger c_{1\alpha} + c_{2\alpha}^\dagger c_{3\alpha} + c_{3\alpha}^\dagger c_{2\alpha} + c_{3\alpha}^\dagger c_{1\alpha} + c_{1\alpha}^\dagger c_{3\alpha} \big] + \varepsilon \big[c_{1\alpha}^\dagger c_{1\alpha} + c_{2\alpha}^\dagger c_{2\alpha} + c_{3\alpha}^\dagger c_{3\alpha} \big] \Big\}$$

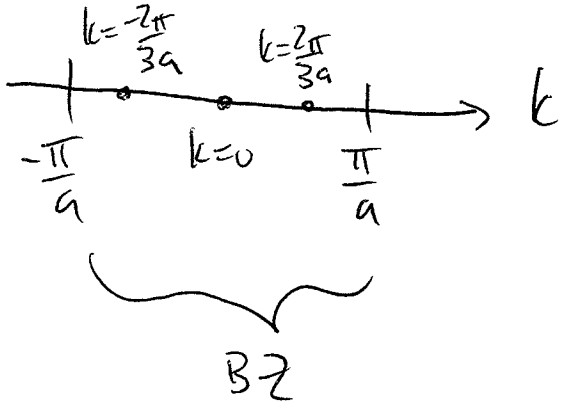
$$= \sum_{\alpha=\uparrow,\downarrow} \begin{pmatrix} c_{1\alpha}^\dagger & c_{2\alpha}^\dagger & c_{3\alpha}^\dagger \end{pmatrix} \begin{pmatrix} \varepsilon & -t & -t \\ -t & \varepsilon & -t \\ -t & 0 & \varepsilon \end{pmatrix} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ c_{3\alpha} \end{pmatrix}$$

(c) The Hamiltonian is invariant under a cyclic permutation $(1\ 2\ 3) \to (2\ 3\ 1)$ of the site index j. This is a consequence of the 120° rotation symmetry of the H_3^+ cation. It is formally equivalent to the translation symmetry of a 3-site system arranged as a linear chain with periodic boundary conditions



In other words, we expect the eigenstates to be states of definite circulation (or angular momentum). This circulation must be in 1-1 correspondence with crystal momentum in the 3-site chain





$\Rightarrow$ circulation eigenvalues $\left\{ \phi_1 = 0,\ \phi_2 = \frac{2\pi}{3},\ \phi_3 = -\frac{2\pi}{3} \right\}$

and $c_{j\alpha} = \frac{1}{\sqrt{3}} \sum_{n=1,2,3} e^{i\phi_n (j-1)} d_{j\alpha}$ $\quad \left(\text{cf. } \frac{1}{\sqrt{N}} \sum_k e^{ikr_j} c_{k\alpha} \right)$

i.e. $$\begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ c_{3\alpha} \end{pmatrix} = \frac{1}{\sqrt{3}} \underbrace{\begin{pmatrix} e^{i\phi_1(0)} & e^{i\phi_2(0)} & e^{i\phi_3(0)} \\ e^{i\phi_1(1)} & e^{i\phi_2(1)} & e^{i\phi_3(1)} \\ e^{i\phi_1(2)} & e^{i\phi_2(2)} & e^{i\phi_3(2)} \end{pmatrix}}_{U} \begin{pmatrix} d_{1\alpha} \\ d_{2\alpha} \\ d_{3\alpha} \end{pmatrix}$$

$$U = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ 1 & e^{i2\pi/3} & e^{-i2\pi/3} \\ 1 & e^{-i2\pi/3} & e^{i2\pi/3} \end{pmatrix}$$

This is a unitary transformation ($\det U = 1$) with inverse

$$U^{-1} = U^{\dagger} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ 1 & e^{-i2\pi/3} & e^{i2\pi/3} \\ 1 & e^{i2\pi/3} & e^{-i2\pi/3} \end{pmatrix}$$

Then $\hat{H}_0 = \sum_{\alpha} c_{\alpha}^{\dagger} \begin{pmatrix} +\varepsilon & -t & -t \\ -t & +\varepsilon & -t \\ -t & -t & +\varepsilon \end{pmatrix} c_{\alpha}$

$$= \sum_{\alpha} d_{\alpha}^{\dagger} U^{\dagger} \begin{pmatrix} \varepsilon & -t & -t \\ -t & \varepsilon & -t \\ -t & -t & \varepsilon \end{pmatrix} U d$$

check that this $= \mathrm{diag}(E_1, E_2, E_3)$

$$\frac{1}{\sqrt{3}}\begin{pmatrix} \varepsilon & -t & -t \\ -t & \varepsilon & -t \\ -t & -t & \varepsilon \end{pmatrix}\begin{pmatrix} 1 & 1 & 1 \\ 1 & z & z^* \\ 1 & z^* & z \end{pmatrix} \quad \text{where } z = e^{i2\pi/3}$$

$$\left(z^* z = 1 \text{ and } z^2 = z^*\right)$$

$$\text{and } 1 + z^* + z = 0$$

$$= \frac{1}{\sqrt{3}}\begin{pmatrix} \varepsilon - 2t & \varepsilon - t(z+z^*) & \varepsilon - t(z+z^*) \\ -t+\varepsilon+t- & -t+\varepsilon z+t- & -t+\varepsilon z^*+t- \\ -t+\varepsilon+t- & -t+\varepsilon z^*+t- & -t+\varepsilon z+t- \end{pmatrix}$$

$$\frac{1}{3}\begin{pmatrix} 1 & 1 & 1 \\ 1 & z^* & z \\ 1 & z & z^* \end{pmatrix}\begin{pmatrix} \varepsilon - 2t & \varepsilon - t(z+z^*) & \varepsilon - t(z+z^*) \\ \varepsilon - 2t & z[\varepsilon - t(z+z^*)] & z^*[\varepsilon - t(z+z^*)] \\ \varepsilon - 2t & z^*[\varepsilon - t(z+z^*)] & z[\varepsilon - t(z+z^*)] \end{pmatrix}$$

$$= \frac{1}{3}\begin{pmatrix} 3(\varepsilon - 2t) & 0 & 0 \\ 0 & 3(\varepsilon + t) & 0 \\ 0 & 0 & 3(\varepsilon + t) \end{pmatrix}$$

i.e. $$\hat{H}_0 = \sum_{\alpha}\sum_{n=1}^{3} E_n d_{n\alpha}^{\dagger} d_{n\alpha}$$

where $E_1 = \varepsilon - 2t$

$E_2 = \varepsilon + t$

$E_3 = \varepsilon + t$

(d) $j=1,2,3$ is a site label for $c_{j\alpha}, c_{j\alpha}^\dagger$

$n=1,2,3$ for $d_{n\alpha}, d_{n\alpha}^\dagger$ is an eigenmode index labelling circulation and eigenenergy

$n=1 \Rightarrow \phi_1 = 0, \; E_1 = \varepsilon - 2t$ } ground state

$n=2 \Rightarrow \phi_2 = \frac{2\pi}{q}, \; E_2 = \varepsilon + t$

$n=3 \Rightarrow \phi_3 = -\frac{2\pi}{q}, \; E_3 = \varepsilon + t$

} degenerate right- and left-circulating excited states

(e) Since the particles are fermions, the lowest-lying state can accomodate one spin-up and one spin-down

$$|\psi_0\rangle = d_{1\uparrow}^\dagger d_{1\downarrow}^\dagger |\text{vac}\rangle$$

$$\hat{H}_0 |\psi_0\rangle = \sum_{n=1,2,3} \sum_{\alpha=\uparrow,\downarrow} E_n d_{n\alpha}^\dagger d_{n\alpha} d_{1\uparrow}^\dagger d_{1\downarrow}^\dagger |\text{vac}\rangle$$

$$= 2E_1 |\psi_0\rangle$$

ground state energy is $2\varepsilon - 4t$

(f) For three electrons on two sites, we expect an average occupation of 2/3 on each site.

$$\langle \psi_0 | \hat{n}_j | \psi_0 \rangle = \sum_{\alpha=\uparrow,\downarrow} \langle \psi_0 | c_{j\alpha}^\dagger c_{j\alpha} | \psi_0 \rangle$$

$$= \sum_{\alpha=\uparrow,\downarrow} \sum_{\substack{n,m \\ =1,2,3}} U_{j,n}^* U_{jm} \langle \psi_0 | d_{n\alpha}^\dagger d_{m\alpha} | \psi_0 \rangle$$

Fermi Sea: $n=3$ —, $n=2$ —, $n=1$ ~~—~~

$d_{n\alpha}^\dagger$ | $d_{m\alpha} | \psi_0 \rangle$: $\delta_{nm}\,\theta(n \le 1)$

$$= 2 |U_{j,1}|^2 = 2\left(\frac{1}{\sqrt{3}}\right)^2 = \frac{2}{3}$$

2(a) $c = Ud \Rightarrow d^\dagger U^\dagger = c^\dagger \Rightarrow d^\dagger = c^\dagger U$

$$(d_{1\alpha}^\dagger \; d_{2\alpha}^\dagger \; d_{3\alpha}^\dagger) = (c_{1\alpha}^\dagger \; c_{2\alpha}^\dagger \; c_{3\alpha}^\dagger) \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ 1 & e^{i2\pi/3} & e^{-i2\pi/3} \\ 1 & e^{-i2\pi/3} & e^{i2\pi/3} \end{pmatrix}$$

i.e. $d_{1\alpha}^\dagger = \frac{1}{\sqrt{3}} (c_{1\alpha}^\dagger + c_{2\alpha}^\dagger + c_{3\alpha}^\dagger)$

$$d_{2\alpha}^\dagger = \frac{1}{\sqrt{3}} (c_{1\alpha}^\dagger + e^{i2\pi/3} c_{2\alpha}^\dagger + e^{-i2\pi/3} c_{3\alpha}^\dagger)$$

Singlet state

$$|\psi^{S=0}\rangle = d_{1\uparrow}^\dagger d_{1\downarrow}^\dagger |vac\rangle$$

n=3 —
n=2 —
n=1 ↑↓

triplet state

$$|\psi^{S=1}\rangle = d_{1\uparrow}^\dagger d_{2\uparrow}^\dagger |vac\rangle$$

n=3 —
n=2 ↑
n=1 ↑

Since $\hat{H}_1 = U \sum_j \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}$ measures electrons in the $c_j, c_j^\dagger$ basis, let's expand $|\psi^{S=0}\rangle$ and $|\psi^{S=1}\rangle$.

$$|\psi^{S=0}\rangle = \frac{1}{3}\left(c_{1\uparrow}^{\dagger} + c_{2\uparrow}^{\dagger} + c_{3\uparrow}^{\dagger}\right)\left(c_{1\downarrow}^{\dagger} + c_{2\downarrow}^{\dagger} + c_{3\downarrow}^{\dagger}\right)|\text{vac}\rangle$$

$$= \frac{1}{3}\left(|\uparrow\downarrow,0,0\rangle + |\uparrow,\downarrow,0\rangle + |\uparrow,0,\downarrow\rangle + |\downarrow,\uparrow,0\rangle + |0,\uparrow\downarrow,0\rangle + |0,\uparrow,\downarrow\rangle + |\downarrow,0,\uparrow\rangle + |0,\downarrow,\uparrow\rangle + |0,0,\uparrow\downarrow\rangle\right)$$

So $\hat{H}_1|\psi^{S=0}\rangle = \frac{1}{3}U\left(|\uparrow\downarrow,0,0\rangle + |0,\uparrow\downarrow,0\rangle + |0,0,\uparrow\downarrow\rangle\right)$

and $\langle\psi^{S=0}|\hat{H}_1|\psi^{S=0}\rangle = \frac{U}{9}\left(\langle\uparrow\downarrow,0,0|\uparrow\downarrow,0,0\rangle + \langle 0,\uparrow\downarrow,0|0,\uparrow\downarrow,0\rangle + \langle 0,0,\uparrow\downarrow|0,0,\uparrow\downarrow\rangle\right)$

$$= \frac{U}{3}$$

$$|\psi^{S=1}\rangle = \frac{1}{3}\left(c_{1\uparrow}^{\dagger} + c_{2\uparrow}^{\dagger} + c_{3\uparrow}^{\dagger}\right)\left(c_{1\uparrow}^{\dagger} + e^{i2\pi/3}c_{2\uparrow}^{\dagger} + e^{-i2\pi/3}c_{3\uparrow}^{\dagger}\right)|\text{vac}\rangle$$

$$= \frac{1}{3}\left(e^{i2\pi/3}c_{1\uparrow}^{\dagger}c_{2\uparrow}^{\dagger} + e^{-i2\pi/3}c_{1\uparrow}^{\dagger}c_{3\uparrow}^{\dagger} + c_{2\uparrow}^{\dagger}c_{1\uparrow}^{\dagger} + e^{-i2\pi/3}c_{2\uparrow}^{\dagger}c_{3\uparrow}^{\dagger} + c_{3\uparrow}^{\dagger}c_{1\uparrow}^{\dagger} + e^{i2\pi/3}c_{3\uparrow}^{\dagger}c_{2\uparrow}^{\dagger}\right)|\text{vac}\rangle$$

$$= \frac{1}{3}\left(\left(e^{i2\pi/3} - 1\right)|\uparrow,\uparrow,0\rangle + \left(e^{-i2\pi/3} - 1\right)|\uparrow,0,\uparrow\rangle + \left(e^{-i2\pi/3} - e^{i2\pi/3}\right)|0,\uparrow,\uparrow\rangle\right)$$

and

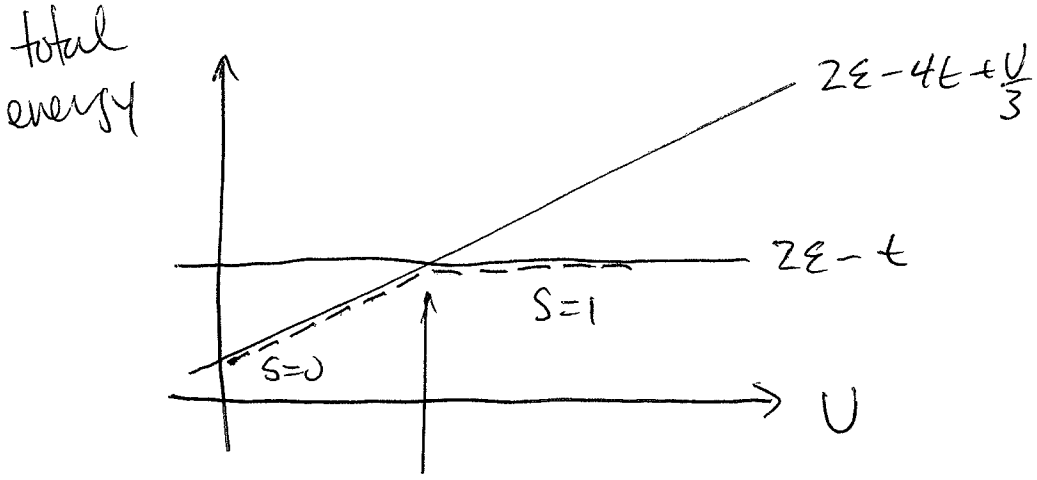
$$\hat{H}_1 |\psi^{S=1}\rangle = 0$$

(b) $$\langle \psi^{S=0} | (\hat{H}_0 + \hat{H}_1) | \psi^{S=0} \rangle = 2E_1 + \frac{U}{3}$$

$$= 2(\varepsilon - 2t) + \frac{U}{3} = 2\varepsilon - 4t + \frac{U}{3}$$

$$\langle \psi^{S=1} | (\hat{H}_0 + \hat{H}_1) | \psi^{S=1} \rangle = E_1 + E_2$$

$$= \varepsilon - 2t + \varepsilon + t = 2\varepsilon - t$$

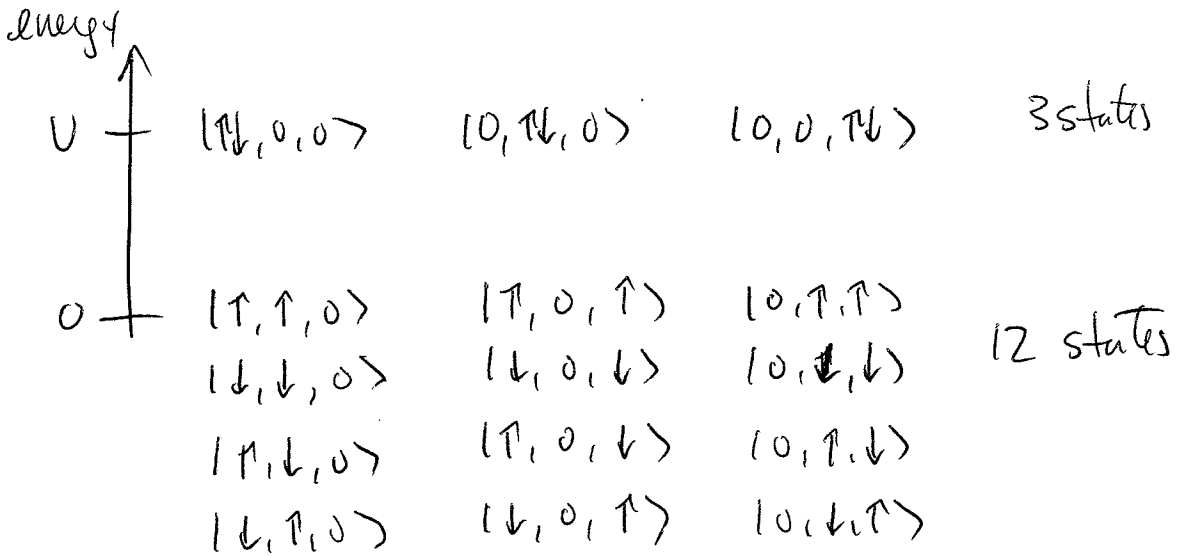


Level crossing at a critical value of the repulsion strength

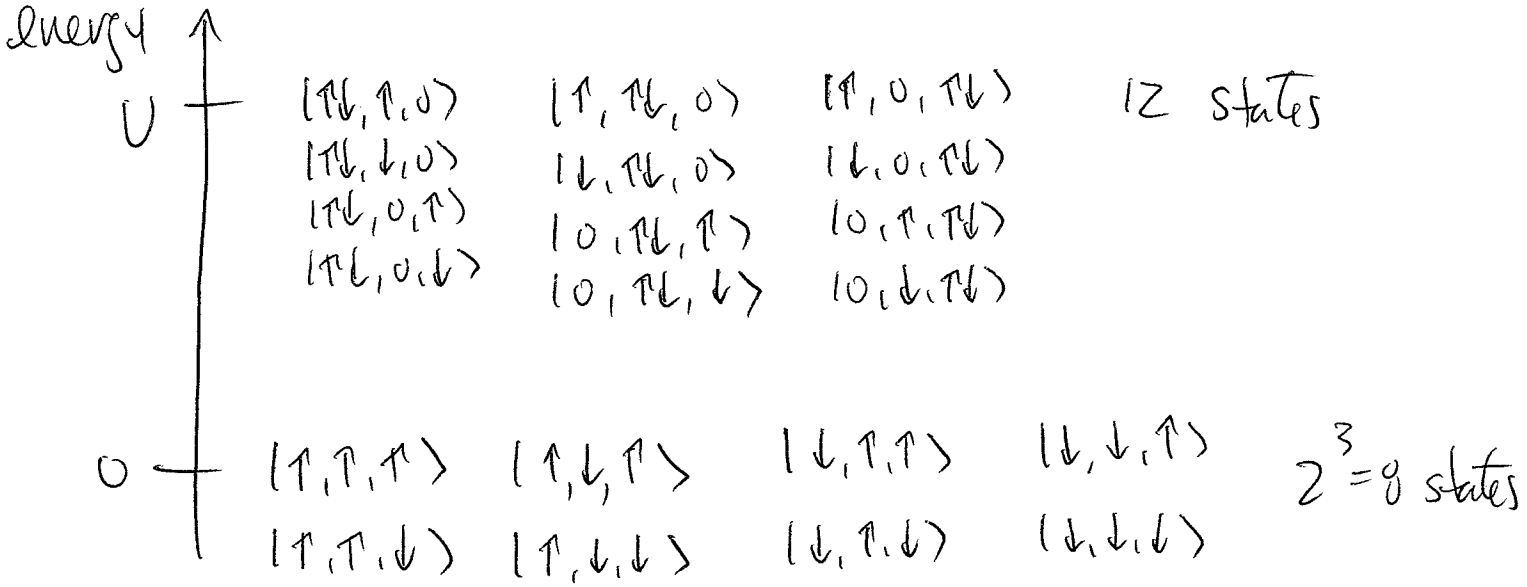
$$2\varepsilon - 4t + \frac{U_c}{3} = 2\varepsilon - t$$

$$\Rightarrow U_c = 9t$$

(c) In the limit $U \to \infty$, the three doubly occupied states move to high energy. All the rest sit at zero



(d) For three electrons,



First order perturbation theory fails to break the ground state degeneracy.

$$\langle \psi | \hat{H}_0 | \psi \rangle = 3\varepsilon$$

for each of the 8 states

But at second order, we can distinguish contributions with aligned and antialigned neighbours:

$$|\uparrow\uparrow\uparrow\rangle \xrightarrow{\hat{H}_{hop} = H_0 - 3\varepsilon \hat{\mathbb{1}}} 0 \quad \text{by Pauli exclusion}$$

$$|\uparrow\downarrow\uparrow\rangle \xrightarrow{\hat{H}_{hop}} |0\uparrow\downarrow\uparrow\rangle \xrightarrow{H_{hop}} |\uparrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\rangle$$

$$-t \cdot \frac{1}{U} \cdot -t$$

exchange process $\sim J = \frac{t^2}{U}$